

Comment on "Surface photovoltages due to pulsed sources: Implications for photoemission spectroscopy", by C.M. Aldao, J.F. Valtuena, I. Izpura, and E. Munoz

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The paper by Aldao et al.¹ corrects an error in my publication "Time dependence of photovoltaic shifts in photoelectron spectroscopy of semiconductors"² That work was based on the argument that carrier mobility is usually large enough to respond to the time structure of synchrotron radiation sources, typically in the MHz range. After publication I realized that, while the response time was adequate, there simply were not enough photons in each pulse to measurably affect the barrier height. This conclusion and a correct treatment were subsequently presented orally³ but, lacking experimental verification, were never published. I was pleased to see the Aldao et al. work correct my original oversight, backed by impressive experimental data.

Though I agree completely with the treatment in reference 1, I offer an additional observation from my own approach. I was concerned at the time about the assumption that the steady state potential could be determined by ignoring the time structure entirely and replacing the photon flux with its average value. I was able to convince myself of this with the following argument.

Suppose the light is on for a time Δt_{on} , then off for a time Δt_{off} . During each on-cycle, the observed potential increases from V_o to $V_i = V_o + \Delta V$. If the system is in steady state, it will decrease again to V_o during the off cycle. We can then write:

$$(1) \quad \Delta t_{on} = \int_{V_i}^{V_o} \frac{C(V)}{(J_{sb}(V) - J_{ph})} dV$$

$$(2) \quad \Delta t_{off} = \int_{V_o}^{V_i} \frac{C(V)}{J_{ph}} dV$$

where J_{ph} is the photocurrent, J_{sb} the restoring current, and C the capacitance of the Schottky barrier.

Each of these integrals can easily be numerically solved for ΔV as a function of V_o , using the relationships in reference 4. The intersection of the two curves gives the steady state values. The result in figure 1 is typical. It shows a negligible change in photovoltage during the pulse, in complete agreement with Aldao et al. In this case, C and J can be approximated to be constant during the pulse, and we can solve equations 1 and 2 to get:

$$(3) \quad \Delta V \approx \frac{J_{sb} - J_{pc}}{C} \Delta t_{on} \approx \frac{J_{sb}}{C} \Delta t_{off}$$

It follows that by defining the average photocurrent as

$$(4) \langle J_{pc} \rangle = J_{pc} \left(\frac{\Delta t_{on}}{\Delta t_{on} + \Delta t_{off}} \right) = J_{sb}$$

we recover the same condition as for continuous illumination, as argued by Aldao et al.

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¹ C.M. Aldao, J.F. Valtuena, I. Izpura, and E. Munoz, Phys. Rev. **B50**, p. 17729, 1994

² M. H. Hecht, Phys. Rev. **B43**, p. 12102, 1991.

³ M. H. Hecht, "Surface Photovoltage Effects in Schottky Barriers Associated with Periodic X-Ray Sources," National Symposium of the American Vacuum Society, Seattle, WA, Nov. 14, 1991.

⁴ M. H. Hecht, Phys. Rev. **B41**, p. 7918, 1990.

Figure 1: Calculated change in magnitude of photovoltage per cycle vs. the average photovoltage assuming a photocurrent of $J_{pc}=10^{-6}$ A/cm² from a 10 MHz pulsed source with a duty cycle of 0.1%. The upper curve corresponds to the *off* cycle, and the lower curve the *on* cycle. The steady state condition, determined from the intersection of the curves, corresponds to a photovoltage of less than 5 millivolts, with a fluctuation due to the pulsed radiation of less than a *microvolt*. The calculation was for room temperature *p*-type GaP, $N_A=3 \times 10^{17}$, and an equilibrium barrier height of $V_b=0.75$ eV.

